-- M A N G A N E S E --

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-- M A N G A N E S E --

Manganese dioxide (pyrolusite) was confused with iron ore until 1740 when Pott showed that it contained no iron. Scheele proved that pyrolusite contained a new element in 1774 and Gahn was the first to isolate the metal itself.

Manganese is valuable in the metallurgy of iron to increase its hardness and heat resistance. It has been very valuable in the manufacture of helmets. Manganese compounds are used for oil dryers, dyes, and in the manufacture of chlorine and oxygen.

In 1837, Couper reported the first case of chronic poisoning by manganese dioxide of a worker who was engaged in crushing the mineral. In the early part of the twentieth century Von Jaksch, Embden and Friedel in separate investigations described the symptoms of poisoning due to manganese containing dusts. Since that time, industry has instituted measures to eliminate the danger of maganese poisoning among its workers.

GENERAL INFORMATION

CHEMICAL FORMULA AND SYNONYMS:

(Manganese) Mn.

(Pyrolusite) MnO_2, manganese dioxide, black.

PROPERTIES:

(Manganese) A reddish-gray or silvery, brittle metallic element. Sp. gr. 7.2 at 20°C.; m. p. 1,260°C.; b. p. 1,900°C. Decomposes water.

(Pyrolusite) Iron black to dark steel-gray or bluish mineral; streak, black or bluish-black; luster, metallic or dull. Sufficiently soft to soil the fingers. Contains 63.2% manganese. Sp. gr. 4.73 to 4.86; hardness 2 to 2.5. Soluble in hydrochloric acid.

OCCURRENCE:

(Manganese) Never found native. Important manganese ores are pyrolusite, braunite, manganite, psilomelane, rhodonite, wad. Manganiferous iron, silver and zinc ores also important. Principal sources of ores: United States, Russia, India, Brazil, West Africa.

(Pyrolusite) United States (Virginia, Georgia, Arkansas, Lake Superior Region, Massachusetts, Vermont, New Mexico), Germany, Bohemia, Transylvania, Austria, India, and Canada.

PREPARATION:

(Manganese) By reduction of the oxide with aluminum or carbon.

IMPORTANT COMPOUNDS:

(Manganese) Manganese acetate, manganese borate, manganese carbonate, manganese chloride, manganese citrate, manganese dioxide, manganese glycerophosphate, manganese hypophosphite, manganese iodide, manganese lactate, manganese-lead resinate, manganese linoleate, manganese monoxide, manganese oleate, manganese oxalate, manganese oxide, manganese peptonate, manganese resinate, manganic hydroxide, manganin, manganite, manganous fluoride, manganous ortho-phosphate, manganous oxide, manganous silicate, manganous sulfate, potassium permanganate.

USES:

(Manganese) Manufacturer of steel (deoxidizer); iron, copper and aluminum alloys; chemicals.

(Pyrolusite) Preparation of manganese.

INDUSTRIAL HEALTH ASPECTS

MODES OF ENTRANCE: Inhalation.

SYMPTOMS OF INDUSTRIAL POISONING: The symptoms of manganese poisoning are generally associated with the inhalation of its oxides and primarily concerned with affections of the central nervous system. The effect of manganese is said to be cumulative and the symptoms usually appear only after several months of exposure. They are evidenced by a peculiar slapping gait, weakness in legs and tremors of the whole body or extremities. Other symptoms frequently observed are mask-like face, impulsive and uncontrollable laughter, disturbances of speech, languor and sleepiness, cramps and stiffness of the muscles, propulsion and retropulsion, and exaggeration of the reflexes.

It is said that manganese, unlike lead, produces no life shortening degenerations. Seriously poisoned victims are life long cripples and often unfit for any gainful employment. The metal apparently makes a very definite attack upon some non-vital portion of the neuro-muscular system, destroys it thoroughly if there has been sufficient exposure, and leaves the victims relatively well in every other respect.

INDUSTRIES AND OCCUPATIONS

INDUSTRIES: Ohio Industries using manganese as indicated in the Ohio Industrial Hygiene Survey are listed as follows:

Automobile factories
Blast furnaces
Brass factories
Brick, tile, and terra cotta
Dyestuffs, ink, etc.
Electric fixtures
Foundries
Glass factories
Other chemicals
Paint and varnish factories
Patent medicine, drugs
Potteries
Storage batteries
Tin and enameled ware

OCCUPATIONS: Occupations in Ohio where contact with manganese was indicated are listed as follows:

Annealers (foundries)
Beaders (tin and enameled ware)
Bin room attendants (storage batteries)
Blenders (paint & varnish factories)
Bluers (automobile factories)
Bottom makers (blast furnaces)
Centrifugal operators (paint & varnish factories)
Chemical engineers (paint & varnish factories)
Chemists (brick, tile and terra cotta; paint & varnish factories)
Closers (paint & varnish factories)
Cupola tenders (foundries)
Decorators (potteries)
Die and tool makers (foundries)
Dippers (potteries; tin and enameled ware)
Dry cell paste mixers (storage batteries)
Dry pan feeders (potteries)
Enamel and paint makers (paint and varnish factories; tin and enameled ware)
Fettlers (potteries)
Fillers (paint & varnish factories; glass factories; patent medicine, drugs)
Filter pressmen (paint & varnish factories)
Firemen (brick, tile and terra cotta)
Foremen (paint & varnish factories)
Foundry laborers (brass factories)
Furnace room laborers (glass factories)
Furnace tenders (brass factories; foundries)
Glazers (potteries)
Glaze preparers (potteries)
Grinders (other chemicals; paint & varnish; electric fixtures; storage batteries)
Handy men (paint & varnish factories)
Heaters (foundries)
Heat treaters (foundries)
Labelers (patent medicine, drugs)
Labelers (blast furnaces; potteries; glass factories; tin and enameled ware; patent medicine, drugs)
Laboratory assistants (paint and varnish factories)
Ladelers (glass factories)
Loaders (brick, tile, terra cotta)
Machine operators (electric fixtures; foundries)
Melters (brass factories; foundries; glass factories)
Mill hands (dyestuffs, ink, etc.)
Mixers (foundries; other chemicals; storage batteries; paint & varnish factories; tin & enameled ware)
Molders (brass factories)
Open hearth men (blast furnaces)
Packers (glass factories)
Painters (foundries; brick,tile, terra cotta; glass factories)
Paint mixers (foundries; paints & varnishes)
Porcelain mixers (tin and enameled ware)

Porcelain sprayers (tin and enameled ware)
Sealers (storage batteries)
Shaders (paint and varnish factories)
Shake-out men (brass factories)
Shipping clerks (glass factories)
Smelters (tin and enameled ware)
Sprayers (potteries; brick, tile and terra cotta)
Tampers (storage batteries)
Testers (paint and varnish factories)
Thinners (paint and varnish factories)
Tinters (paint and varnish factories)
Transfer men (brick, tile & terra cotta)
Truckers (dyestuffs, ink, etc.)
Varnish makers (paint and varnish factories)
Washers (automobile factories)
Weighers (foundries; paint and varnish factories; dyestuffs, ink, etc.)
Wrappers (storage batteries)

Occupations which offer contact with manganese but not listed in the Ohio Survey are:*

Battery makers
Bleaching powder makers
Calico printers
Chlorine makers
Dye makers
Dyers
Enamelers
Fertilizer makers
Fireworks makers
Glass mixers
Linoleum makers
Manganese dioxide workers
Match factory workers
Soap makers
Varnishers
Zinc miners

*Dublin, L.I., and Vane, R.J.: Occupation Hazards and Diagnostic Signs. U.S. Department of Labor, Bureau of Labor Statistics, Bulletin No. 582:40, 1933.

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INDUSTRIAL MANGANESE POISONING-WITH A REVIEW OF THE LITERATURE.

Wm. D. McNally. Indust. Med., vol. 4, p. 581, (1935).

Abstracted in J. of Ind. Hygiene, vol. 18, no. 4, p. 49 (abstract section) April 1936.

The author gives a detailed chronological review of 131 cases of chronic manganese poisoning, and in addition, the detailed history of 1 case of manganese poisoning, observed by himself. His patient was exposed to dust of manganese ores as used in the manufacture of batteries. The first symptoms were slight motor disturbances, and subsequently, fatigue, excitement, and tremors of the right leg developed. In the course of half a year the neurological symptoms became decidedly more marked and at this time the degenerative changes were seen not only in the lower extremities but also in the upper extremities and the ocularmotor apparatus. A short discussion of the prophylactic measures for the prevention of such poisonings and the pathology of manganese poisoning are given. Directions for the detection of manganese in urine and blood and a discuaaion of the treatment of the conditions conclude this report.--W.F. von Oettingen.

MANGANESE: ITS DISTRIBUTION, PHARMACOLOGY AND HEALTH HAZARDS.

W.F. von Oettingen. Physiol. Rev., Apr. 1935, vol. 15, pp. 175-201.

Abstracted in J. of Ind. Hygiene, vol. 17, no. 6, p. 124 (abstract section) Nov. 1935.

This is an excellent review with a very complete bibliography and pertinent tables summarizing experimental work on manganese poisoning, the distribution of manganese in biological matter, and an analysis of reports on cases of manganese poisoning in man.--Philip Drinker.

A NEW METHOD FOR THE MICRODETERMINATION OF MANGANESE IN BIOLOGICAL MATERIALS.

A.C. Wiese and B. Connor Johnson. J. Biol. Chem. 127, 203-9 (1939).

Abstracted in J. of Ind. Hygiene, vol. 22, no. 1, p. 22 (abstract section) Jan. 1940.

The microdetn. of Mn is based upon the oxidation of benzidine by permanganate in the presence of HNO_3. The yellow-green color is read with the photoelec. colorimeter with a 4200 A. filter. It is possible to perform 6-8 filtrations through the same filter and then read the colors developed, in this way reading 30-40 dotns, in an hr. From 0.1 to 100 gamma of Mn can be estd. and recoveries range from 92 to 106%.

EXPERIMENTAL MANGANESE POISONING.

A.M. Grunstein and N. Popowa. Abstr. as follows from Arch. f. Psychiat., July, 1929, vol. 87, p. 742, in Arch. Neurol. and Psychiat., June, 1930, vol. 23, p. 1275.

Abstracted in J. of Ind. Hygiene, vol. 12, no. 10, p. 221 (abstract section) Dec. 1930.

The authors report the results of clinical and anatomic observations of rabbits subjected to the effects of powdered manganese. They begin with a discussion of the literature, which they sum up as follows: In the reported cases of manganese poisoning in man, the clinical picture consisted

of muscular rigidity, mask-like facies, compulsive laughing and crying, increased salivation, tremors, and disturbances of gait. These symptoms altogether usually presented a parkinson-like picture, so that it could be assumed that the pathologic process would be mainly localized in the globus pallidus. So far, however, no anatomic observations in such cases have been reported. Experimentally, observations of this type have been studied in animals of different types (Mella in this country studied the effects of manganese poisoning in monkeys).

The observations of the authors are essentially similar to those of other observers, and the results are summed up as follows: Clinically, the symptoms varied from episodic paralyses of the hind legs to general weakness of the musculature without any definite neurologic changes. Anatomically, marked changes of the central nervous system were found in the form of advanced degenerative phenomena of the nerve cells. These were particularly intense in the small cells of the caudate nucleus and putamen, but were observed also in the pallidum and in some parts of the cortex. In some cases there were, in addition to these changes, proliferations of the neroglia and lesions in the walls of blood vessels, as well as degeneration in the cells of the choroid plexus. There were marked degenerative lesions in the liver, spleen, heart, kidneys, and suprarenal glands.

ANIMAL EXPERIMENTS ON LUNG CHANGES AFTER MANGANESE DUST INHALATION.

H. Reploh. Arbeitsschutz, pp. 144-146 (1939).

Abstracted in J. of Ind. Hygiene, vol. 21, no. 6, p. 146 (abstract section) June 1939.

The author had rabbits and mice inhale dust containing 90% MnO_2. Of 32 animals employed, 9 died in the first 19 days, all of which showed more or less pronounced bronchopneumonia. Of the surviving animals 16 were infected intranasally with pneumococci and half of them were then exposed 15 minutes a day to drafts and cold. Three of the animals only dusted survived, but only one that was infected with pneumococci and 2 infected and exposed to cold. These last two had the most marked lung changes. Among the mice the ones only dusted had no changes. Since Thomas slag induces pneumonia in man also, the author experimented with dust containing 10% MnO_2 to simulate Thomas slag. Of 23 rabbits exposed, 7 died during inhalation, three of which showed clear lung changes. Later 13 animals were infected with pneumococci and the three that died showed very severe changes. Mn dust injected into the abdomen evoked a fibrinous suppurative hemorrhagic peritonitis. The author believes the pneumonia caused by Thomas slag dust may be traced to the MnO_2.--L. Teleky.

PROGRESSIVE BULBAR PARALYSIS AND AMIOTROPHIC LATERAL SCLEROSIS AFTER CHRONIC MANGANESE POISONING.

H. Voss. Arch. f. Gewerbepath., vol. 9, pp. 454-476 (1939).

Abstracted in J. of Ind. Hygiene, vol. 21, no. 9, p. 214 (abstract section) Nov. 1939.

A careful clinical, anatomical and histological description of a case of progressive bulbar paralysis and amiotrophic lateral sclerosis, which developed in a man who worked 15 yrs. with MnO_2. The author thinks (correctly) that the manganese intoxication was partly responsible for

this disease. The poisoning befell a man disposed to lateral sclerosis and produced a lateral sclerosis modified by certain symptoms of manganese poisoning.--L. Teleky.

THE DIAGNOSIS OF INDUSTRIAL POISONING DUE TO MANGANESE.

J. Leclercq. Arch. Gewerbepath. u. Gewerbehyg., Sept. 1934, vol. 5, pp. 337-344.

Abstracted in J. of Ind. Hygiene, vol. 17, no. 2, p. 23 (abstract section) March 1935.

A picture is given of poisoning by manganese resulting from occupational exposure to its dust and fumes. Manganese is used metallurgically in making steel and such metals as copper, zinc, bronze, nickel and aluminium. It is also used in making glass, colors and varnish, pottery, and electric batteries. The portal of entry is said to be the digestive tract rather than the lungs, while the skin can be disregarded. The poisonous dose has not been determined, but years of exposure seem required before any symptoms appear, slowly and insidiously. The nervous system is peculiarly affected; and a clinical condition similar to Parkinson's disease is established. Once established no improvement can be obtained, although the progress of the disease may be suspended by cessation of exposure to risk. While this article is based upon personal experience (the exact extent of which is not stated), no new points arise. The author stresses the probability of cases passing unrecognized to their graves, owing to their insidious onset and rarity, should the medical attendant be unaware of the occupational exposure of the patient.--E.L. Collis.

MANGANESE POISONING.

E.W. Baader. Arch. Mal. Profes., vol. 1, pp. 104-108 (1938).

Abstracted in J. of Ind. Hygiene, vol. 21, no. 4, p. 98 (abstract section) April 1939.

Cases of manganese poisoning from inhaling its dust are comparatively rare, only about 130 having been reported in the literature, with a possibility that some have passed unrecognized. Some predisposition to the poisoning seems to be necessary and the symptoms appear generally during the first 2 years of exposure. The illness begins rapidly and progresses in a few months to a typical and incurable condition. Symptoms usually are: the patient is easily tired and falls to sleep easily; unsteady gait; difficulty in ascending a slope; little control over facial muscles or expression; both speech and writing are protracted and slurred; swallowing may be difficult; and there are sometimes violent pains and muscular cramps.--W.H. Buck.

MANGANESE POISONING.

D. Owen and H. Cowen. Lancet Nov. 3, 1934, pp. 989-990, and Annotation, Ibid., Nov. 10, 1934.

Abstracted in J. of Ind. Hygiene, vol. 17, no. 2, p. 23 (abstract section) March 1935.

References are made to 4 cases of chronic poisoning in men working in the same manganese works. Symptoms appeared in one case after only 8 months' exposure, and in the other three after $2\frac{1}{2}$, $6\frac{1}{2}$, and 8 years. The clinical picture was indistinguishable from chronic post-encephalitic

parkinsonism. No improvement occurred even though contact with manganese ceased for 1 to 2 years General health is hardly impaired; but the patients survive for years in a more or less wretched and crippled state. The whole condition is well summarized in the second reference wherein full appreciation is given to the work done in the United States and announced in this Journal (1919, vol. 1, p. 183).--E.L. Collis.

MANGANESE POISONING CASE.

W.D. McNally. Indust. Med., July 1935, vol. 4, pp. 349-350.

Abstracted in J. of Ind. Hygiene, vol. 17, no. 6, p. 124 (abstract section) Nov. 1935.

The case presented is that of a 29 year old man who worked as a laborer in the ore department of a battery company, transporting, loading, and handling manganese in powdered form. After 14 months' work, he noticed that after dumping a wheelbarrow, he had difficulty in stopping himself when he stepped back. In a week's time this became progressively worse and the man stopped work. There was no change after 6 months by which time he had difficulty in walking, as his gait increased and he would fall unless caught. More recently he has developed a tremor which involves the entire right leg, although there is no tremor in the hands, head, or left leg. Further clinical findings are given, with suggested treatment and points to be especially noted in making a diagnosis of manganese poisoning.--H.N. Lawson.

SERIOUS MANGANESE POISONING AMONG EGYPTIAN MANGANESE MINERS.

E.W. Baader, Arch. f. Gewerbepath., vol. 9, pp. 477-486 (1939).

Abstracted in J. of Ind. Hygiene, vol. 21, no. 9, p. 214 (abstract section) Nov. 1939.

From 1921-1931 and since 1935, manganese ore mines were worked on the Sinai peninsula. Jackhammer drills were introduced in 1931. Egyptian physicians described 26 cases of poisoning and on a recent trip, the author saw some of the cases, which he described here. It is remarkable that some cases show mental disorder at the beginning; furthermore, that at the time of hand drilling, the disease develops only after some years, but with the introduction of mechanical drilling (with terrible amounts of dust), it comes on after 3 weeks to 5 months (average, 3 mos.). Many deaths from pneumonia are noted.--L. Teleky.

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Factory and Workshop Order: Notification of Manganese Poisoning. (Great Britain), July 1936.